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A CONVENIENT SYNTHESIS OF (-)-METHYL EPIJASMONATE

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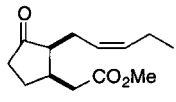
ABSTRACT: A short, enantioselective synthesis of (-)-methyl *epi*-jasmonate, *ent*-**1**, has been achieved starting from readily available Corey lactone aldehyde **9**. The key features include the stereoselective installation of 2,3-*cis*-disubstituted side-chains by hydrogenation of dienoate **8** and subsequent one-carbon degradation.

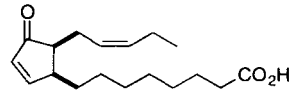
INTRODUCTION

The continuing interest in a plethora of five-membered carbocycles such as prostaglandins, steroids, terpenes, and polyquinanes has resulted in the development of a number of efficient synthetic approaches. More recently, the synthesis of naturally occurring *cis*-2,3-dialkylcyclopentanones has received considerable attention. Representative examples include methyl epijasmonate (**1**),[1,2] 12-oxo-phytodienoic acid (**2**),[3] preclavulone A (**3**),[4] and 8-*epi*-PGE_2 methyl ester (**4**).[5] These "isoprostanes" and structurally related compounds have been shown to exhibit interesting bioactivities. For their preparation care should be undertaken to avoid facile epimerization to the thermodynamically more stable *trans* isomers. Thus, the vicinally *cis*-disubstituted cyclopentanone system is a considerably more challenging synthetic target than its more stable *trans* epimer; not surprisingly, only a handful of syntheses have been reported. As a

preliminary study in this area of "isoprostanes", we decided to undertake an enantioselective synthesis of (-)-methyl *epi*-jasmonate, *ent*-**1**.[6] Our synthesis was guided by the ready availability of an enantiomerically pure starting material.



1



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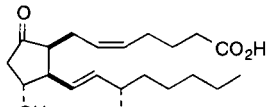

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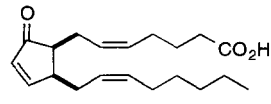
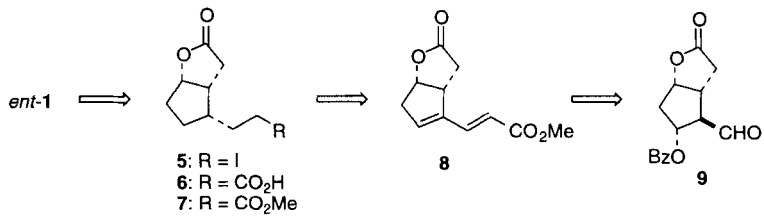


3

RESULTS AND DISCUSSION

Our retrosynthetic analysis (**Scheme 1**) revolved around our key intermediate **6**. We envisioned that its requisite one-carbon degradation of the lower side-chain could be achieved by means of oxidative decarboxylation, followed by oxidation of the resulting iodide **5**.[7,8] At the same time, the stereoselective introduction of the ω-chain of **6** could most conveniently be achieved by hydrogenation of the dienoate **8**, which in turn would be readily available from commercially available Corey lactone aldehyde **9**.[9]

Scheme I



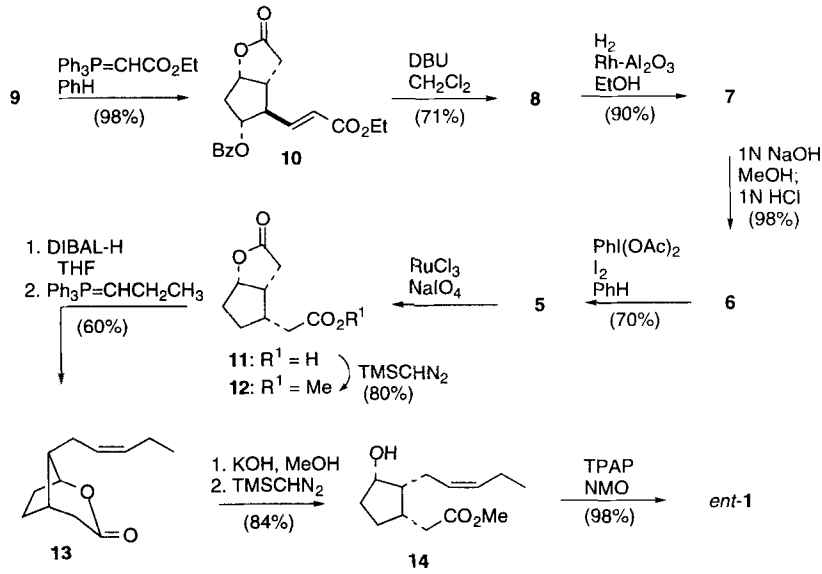
5: R = I
6: R = CO_2H
7: R = CO_2Me

8

9

Thus, our synthesis began with the Wittig olefination of **9** with (carbethoxymethylene)triphenylphosphorane to produce the ester **10** in 98% yield (**Scheme 2**). Subsequent treatment with DBU afforded the dienoate **8** in 71% yield. Hydrogenation (5% Rh–Al_2O_3) of **8** then afforded stereoselectively ester **7** in 90% yield. Ester **7** was then converted to acid **6** by standard methods involving basic hydrolysis (1N NaOH), followed by treatment with 1N HCl. The one-carbon degradation of **6** to the acid **11** was then achieved in the two-step procedure of Suárez.[7] Thus, use of $PhI(OAc)_2$ - I_2 afforded the iodide **5** in 70% yield, and subsequent RuO_4 oxidation[7,10] furnished the acid **11**. The crude acid was then treated with trimethylsilyldiazomethane to give the known methyl ester **12** in 80% overall yield. By utilizing the previously established procedure,[1c,11] **12** was converted by means of the lactone **13** to the alcohol **14** in good overall

Scheme 2



yield. Finally, TPAP oxidation[12] produced (-)-methyl *epi*-jasmonate, whose spectral data and optical rotation are in excellent agreement with those reported in the literature. As judged from its ^{13}C NMR spectrum, *ent*-**1** appeared to be configurationally pure with the absence of the *trans* epimer.

CONCLUSION

In summary, we have developed a short, enantioselective synthesis of (-)-methyl *epi*-jasmonate, *ent*-**1**, by taking advantage of commercially available Corey lactone aldehyde **9**. The salient features include the stereoselective construction of the 2,3-*cis*-disubstituted cyclopentanone system by hydrogenation of dienoate **8** and the one-carbon degradation of the lower side-chain in acid **6** by oxidative decarboxylation and subsequent iodide oxidation. Further synthetic studies of "isoprostanes" are currently in progress.

EXPERIMENTAL SECTION[13]

(1*S*,5*R*)-6-(2'-Carbomethoxy-1'-ethenyl)-2-oxabicyclo[3.3.0]-oct-6-en-3-one (8). A solution of Corey lactone aldehyde (5 g, 18.2 mmol) in benzene (25 mL) was treated with carbethoxymethylenetriphenyl phosphorane (15.8 g, 45.5 mmol). The reaction mixture was stirred at room temperature for 30 min. The solvent was removed *in vacuo*, and purification of the concentrate by SiO_2 column chromatography (using 3:1 to 1:1 hexane-EtOAc as gradient eluents) afforded 6.13 g (98%) of α,β-unsaturated ester **10**.

A solution of **10** (4.58 g,13.3 mmol) in CH_2Cl_2 (20 mL) was treated with DBU (2.2 mL, 14.6 mmol) and a resulting mixture was stirred at room

temperature for 3 h. The solvent was removed *in vacuo*, and purification of the concentrate by SiO_2 column chromatography (using 3:1 hexane-EtOAc as eluent) gave 2.09 g (71%) of **8** as a off-white solid: mp 100-102 °C; $[\alpha]_D = +180.8°$ (*c* 1.3, $CHCl_3$); IR ($CHCl_3$) 1783, 1718 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.2 Hz, 3 H), 2.57 (dd, *J* = 18.3, 2.6 Hz, 1 H), 2.86 (dd, *J* = 18.3, 10.2 Hz, 1 H), 2.82-2.97 (m, 2 H), 3.65 (m, 1 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 5.24 (td, *J* = 6.3, 1.7 Hz, 1 H), 5.71 (d, *J* = 16.1 Hz, 1 H), 6.14 (t, *J* = 2.7 Hz, 1 H), 7.41 (d, *J* = 16.1 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 14.2, 32.1, 40.1, 44.0, 60.7, 82.7, 119.8, 137.1, 138.1, 140.5, 166.5, 176.0; MS *m/z* (rel) 222 (M^+, 28), 194 (13), 177 (50), 149 (77), 132 (100), 121 (98), 105 (50); HRMS (M^+) 222.0892 calcd for $C_{12}H_{14}O_4$, found 222.0874.

(1*S*,5*R*)-6-(2'-Carbomethoxyethyl)-2-oxabicyclo[3.3.0]-oct-6-en-3-one (7). A solution of **8** (1.53 g, 6.89 mmol) in EtOH (21 mL) was hydrogenated over 5 % Rh-Al_2O_3 (310 mg) under an atmospheric pressure of hydrogen until uptake of hydrogen ceased. The catalyst was filtered through the Celite, and the filterate was concentrated *in vacuo* to afford an oil. Purification by SiO_2 column chromatography (using 3:1 hexane-EtOAc as eluent) furnished 1.40 g (90%) of **7**: $[\alpha]_D = +8.1°$ (*c* 3.6, $CHCl_3$); IR (neat) 1730, 1774 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3 H), 1.25-1.35 (m, 1 H), 1.67-1.82 (m, 4 H), 1.88-2.00 (m, 1 H), 2.04 (m, 1 H), 2.32 (dt, *J* = 2.4, 7.3 Hz, 2 H), 2.43 (dd, *J* = 18.7, 5.5 Hz, 1 H), 2.53 (dd, *J* = 18.7, 10.6 Hz, 1 H), 2.97 (m, 1 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 5.03 (t, *J* = 6.6 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 14.1, 25.7, 28.3, 28.4, 32.8, 33.0, 40.2, 41.9, 60.3, 85.7, 172.9, 177.4; MS *m/z* (rel) 226 (M^+, 4), 180 (100), 167 (82), 152 (94), 139 (90); HRMS (M^+) 226.1205 calcd for $C_{12}H_{18}O_4$, found 226.1186.

(1*S*,5*R*)-6-(2'-Carboxyethyl)-2-oxabicyclo[3.3.0]-oct-6-en-3-one (6). A solution of **7** (1.27 g, 5.62 mmol) in MeOH (24 mL) was treated with 12 mL of aqueous 1 N NaOH solution and stirred at room temperature for 3 h. A bulk of methanol was removed *in vacuo*, and the residue was acidified to pH 2 with aqueous 1 N HCl solution. The solvent was then removed in high vacuum to give 1.09 g (98%) of **6** as a white solid: mp 50-52 °C; $[\alpha]_D$ = +10.3° (*c* 1.72, $CHCl_3$); IR ($CHCl_3$) 3330, 1764, 1707 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.25-1.37 (m, 2 H), 1.68-1.84 (m, 3 H), 1.91-2.00 (m, 1 H), 2.06 (m, 1 H), 2.36-2.42 (m, 2 H), 2.43 (dd, *J* = 18.8, 5.3 Hz, 1 H), 2.55 (dd, *J* = 18.8, 10.6 Hz, 1 H), 2.99 (m, 1 H), 5.05 (t, *J* = 6.4 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 25.5, 28.4, 28.6, 32.8, 32.9, 40.3, 41.9, 85.9, 177.7, 179.0; MS *m/z* (rel) 198 (M^+, 10), 152 (100), 139 (99), 121 (61); HRMS (M^+) 198.0892 calcd for $C_{10}H_{14}O_4$, found 198.0872.

(1*S*,5*R*)-6-(2'-iodoethyl)-2-oxabicyclo[3.3.0]-oct-6-en-3-one (5). To a solution of **6** (920 mg, 4.65 mmol) in benzene (500 mL) was added sequentially iodine (590 mg, 2.33 mmol) and iodobenzene diacetate (751 mg, 2.33 mmol). The mixture was refluxed under two 100W tungsten filament lamps for 45 min. An additional portion of iodine (590 mg, 2.33 mmol) and iodobenzene diacetate (751 mg, 2.33 mmol) was then added, and the reaction mixture was then left for an additional 12 h. The mixture was washed with 5% aqueous sodium thiosulfate solution and water. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by SiO_2 column chromatography (using 6:1 hexane-EtOAc as eluent) afforded 911 mg (70%) of **5**: $[\alpha]_D$ = +8.5° (*c* 5.17, $CHCl_3$); IR (neat) 1774 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.24-1.37 (m, 1 H), 1.71-1.85 (m, 2 H), 1.89 (apparent q, *J* = 7.0 Hz, 2 H), 2.04-2.15 (m, 2 H), 2.37 (dd, *J* = 18.6, 5.1 Hz, 1 H), 2.57 (dd, *J* = 18.6, 9.5 Hz, 1 H), 3.01 (m, 1 H), 3.12-3.23 (m, 2 H), 5.06 (t, *J* = 6.2 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 4.3, 27.8,

28.7, 32.6, 34.2, 39.7, 43.0, 85.5, 177.1; MS *m/z* (rel) 281 (M^++H, 70), 280 (M^+, 65), 251 (7), 208 (10), 153 (100), 135 (55), 107 (85); HRMS (M^+) 279.9960 calcd for $C_9H_{13}IO_2$, found 279.9960.

(1*S*,5*R*)-6-Carbomethoxymethyl-2-oxabicyclo[3.3.0]-oct-6-en-3-one (12). To a solution of iodide **5** (750 mg, 2.68 mmol) in CCl_4 (8 mL), MeCN (8 mL), and H_2O (12 mL) were added sequentially $NaIO_4$ (2.33 g, 10.9 mmol) and $RuCl_3 \cdot H_2O$ (28 mg, 0.1 mmol). The mixture was stirred for 12h and cooled to 0 °C. Et_2O (30 mL) was then added, and the resulting mixture was vigorously stirred for 10 min. The organic layer was separated and the aqueous layer was extracted with ether (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure to afford the crude acid **11**. The crude acid was dissolved in benzene (21 mL) and MeOH (6 mL), followed by addition of $TMSCHN_2$ (2.0 M in hexane, 2.68 mL, 5.36 mmol). After the mixture was stirred at room temperature for 30 min, the solvent was removed *in vacuo*. Purification by SiO_2 column chromatography (using 6:1 hexane-EtOAc as eluent) gave 426 mg (80%) of **12**: $[\alpha]_D$ = +20.8° (*c* 1.53, $CHCl_3$); IR (neat) 1734, 1772 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.29-1.39 (m, 1 H), 1.69-1.84 (m, 2 H), 2.01-2.08 (m, 1 H), 2.32-2.46 (m, 4 H), 2.33 (dd, *J* = 18.8, 4.9 Hz, 1 H), 2.54 (dd, *J* = 18.8, 10.8 Hz, 1 H), 3.08 (m, 1 H), 3.67 (s, 3 H), 5.03 (t, *J* = 6.2 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 28.7, 28.9, 32.7, 35.0, 38.7, 40.2, 51.7, 85.7, 172.5, 177.2; MS *m/z* (rel) 198 (M^+, 5), 180 (24), 166 (87), 152 (91), 149 (100), 138 (93), 124 (90), 113 (57); HRMS (M^+) 198.0892 calcd for $C_{10}H_{14}O_4$, found 198.0890.

(1*S*,5*S*,8*R*)-8-[*Z*-2'-Pentenyl]-2-oxabicyclo[3.2.1]-oct-3-one (13). To a solution of **12** (408 mg, 2.06 mmol) in THF (50 mL) at -78 °C was added

dropwise DIBAL-H (1.0 M, 2.16 mL, 2.16 mmol). The mixture was stirred at the same temperature for 3 h, quenched with addition of water (2 mL). Aqueous 1N HCl solution was added until the inorganic precipitate was dissolved. The organic layer was then separated, and the aqueous layer was extracted with ether (3 x 10 mL). The combined extracts were washed with aqueous $NaHCO_3$ solution and brine, and dried over $MgSO_4$. The solvent was removed *in vacuo* to furnish crude lactol (410 mg).

A suspension of *n*-propyltriphenylphosphonium bromide (3.17 g, 8.24 mmol) in THF (80 mL) was treated with $KN(TMS)_2$ (0.5 M, 14.8 mL, 7.42 mmol), and the reaction mixture was stirred at room temperature for 3 h. After the resulting dark red solution was cooled to -78 °C, a solution of the previously obtained lactol in THF (5 mL) was added dropwise. The mixture was stirred at -78 °C for an additional 1 h, allowed to warm to 0 °C, and then quenched with a 30% $NaHSO_3$ solution. The aqueous layer was extracted with hexane. The organic extract was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by SiO_2 column chromatography (using 6:1 hexane-EtOAc as eluent) afforded 240 mg (60%) of **13**: $[\alpha]_D$ = +68.4° (*c* 1.76, $CHCl_3$) [lit.[2c] +65.7° (*c* 1.05, MeOH); lit.[2a] -73.0° (*c* 3.0, $CHCl_3$) for (-)-**13**]; IR (neat) 1732 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.2 Hz, 3 H), 1.72-1.81 (m, 2 H), 1.92-2.41 (m, 9 H), 2.75 (ddd, *J* = 18.9, 5.3, 2.3 Hz, 1 H), 4.60 (m, 1 H), 5.37 (m, 1 H), 5.45 (m, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 14.2, 20.6, 23.2, 30.0, 32.1, 34.3, 36.1, 44.8, 82.2, 125.6, 133.8, 171.0; MS *m/z* (rel) 194 (M^+, 18), 176 (15), 165 (23), 138 (51), 134 (100), 125 (79), 119 (76), 104 (69).

(1*S*,2*R*,5*S*)-3-Carbomethoxymethyl-2-(*Z*-2'-pentenyl)-1-cyclopentanol (14). To a solution of **13** (210 mg, 1.08 mmol) in MeOH (10 mL) and H_2O (1 mL) was added KOH (607 mg, 10.8 mmol). The mixture was stirred at room

temperature for 2 h. After a bulk of methanol was removed under reduced pressure, the aqueous solution was acidified to pH 2 with 1N HCl, extracted with CH_2Cl_2 (3 x 5 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in benzene (8.6 mL) and MeOH (2.1 mL), and then treated with $TMSCHN_2$ (2.0 M in hexane, 1.1 mL, 2.2 mmol). After the resulting mixture was stirred at room temperature for 30 min, the solvents were removed *in vacuo* to provide the crude methyl ester. Purification by SiO_2 column chromatography (using 6:1 hexane-EtOAc as eluent) gave 180 mg (74%) of **14**: $[\alpha]_D$ = -10.8° (*c* 2.38, $CHCl_3$); IR (neat) 3500, 3000, 1735 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.5 Hz, 3 H), 1.43 (d, *J* = 3.3 Hz, 1 H), 1.59-1.75 (m, 2 H), 1.81-1.95 (m, 3 H), 2.05-2.13 (m, 3 H), 2.21-2.30 (m, 1 H), 2.35-2.51 (m, 3 H), 3.67 (s, 3 H), 4.21 (m, 1 H), 5.40 (m, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 14.2, 20.7, 22.9, 29.4, 33.4, 36.4, 36.6, 47.7, 51.4, 74.7, 127.7, 132.6, 174.5; MS *m/z* (rel) 208 (M^+-H_2O, 25), 194 (8), 176 (18), 165 (41), 152 (47), 134 (100), 119 (88).

(-)-Methyl *Epi*-jasmonate (*ent*-1). To a solution of **14** (33 mg, 0.146 mmol) in CH_2Cl_2 (5 mL) were added NMO (51 mg, 0.44 mmol), 4Å molecular sieves (70 mg) and TPAP (2 mg, 0.015 mmol). The mixture was stirred at room temperature for 30 min and filtered through a pad of silica gel. After the solvent was removed, the residue was purified by flash column chromatography (silica gel, 6:1 hexane/EtOAc) to give 32 mg (98 %) of *ent*-**1**: as a colorless oil: $[\alpha]_D$ = -44.8° (*c* 1.42, MeOH) [lit.[14] +50° (*c* 0.14, MeOH) for natural **1**]; IR (neat) 3000, 1739 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.5 Hz, 3 H), 1.82 (m, 1 H), 1.98-2.19 (m, 5 H), 2.21-2.42 (m, 4 H), 2.43 (dd, *J* = 15.6, 5.3 Hz, 1 H), 2.84 (m, 1 H), 3.69 (s, 3 H), 5.21 (m, 1 H), 5.44 (m, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$)[1e,2d] δ 14.0, 20.6, 22.9, 25.6, 33.7, 35.2, 35.5, 51.7, 52.7, 125.4, 133.5,

172.9, 218.9; MS *m/z* (rel) 224 (M^+, 70), 206 (59), 193 (33), 177 (58), 164 (26), 151 (89), 133 (73), 121 (58), 109 (100).

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